

New phenomena in interaction of intense ultrashort light pulses with transparent materials: from 3D self-assembled nanostructures to quill writing and nonreciprocal photosensitivity

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ABSTRACT

Recently a remarkable phenomenon in ultrafast laser processing of transparent materials has been reported manifesting itself as a change in material modification by reversing the writing direction. It has been experimentally demonstrated that the pulse front tilt is responsible for the occurrence of directional dependence. Additionally, an anisotropic cavitation was observed in the vicinity of the focus at high fluences. The bubbles, formed in the bulk of the glass, can be trapped and manipulated in the plane perpendicular to the light propagation direction by controlling the laser writing direction relative to the tilt of the pulse front. Another intriguing effect recently discovered occurs when the direction of the femtosecond laser beam is reversed from +Z to -Z directions, the structures written in a lithium niobate crystal are mirror images when translating the beam along the +Y and -Y directions. In contrast to glass, the directional dependence of writing in lithium niobate depends on the orientation of the crystal with respect to the direction of the beam movement and the light propagation direction. A theoretical model was created to demonstrate how in the lithium niobate, the nonreciprocal photosensitivity manifests itself as a changing the sign of the light-induced current when the light propagation direction is reversed. Therefore, in a non-centrosymmetric medium, modification of the material can be different when light propagates in opposite directions.

Keywords: ultrafast laser direct writing, non-reciprocity, lithium niobate, pulse front tilt, anisotropic cavitation

1. INTRODUCTION

Writing is the main method for information storage, which has been known from the dawn of civilization. These days direct write technologies, including plasma spray, micropen, ink jet, e-beam, focused ion beam and laser beam are of increasing importance in material processing¹. More recently, modification of transparent materials with ultrafast lasers has attracted considerable interest due to a wide range of applications including laser surgery², integrated optics³, optical data storage⁴, and three-dimensional micro-⁵ or nanostructuring⁶. Demonstration of femtosecond laser nano-surgery and optical tweezers made the combination of ultrafast laser processing and optical manipulation very attractive for biophotonic applications^{7, 8}. Moreover, modifications of materials by light span from photosynthesis and photography to material processing and laser writing, and there are only few independent parameters of irradiation which control material transformations, in particular wavelength, intensity, exposure time and pulse duration. For instance, a key advantage of using femtosecond pulses, as opposed to longer pulses, for direct writing is that such pulses can rapidly and precisely deposit energy in solids⁹. The process, initiated by multiphoton ionization, exhibits a highly nonlinear dependence on the intensity of the light beam. The light is absorbed by photoelectrons and the optical excitation ends before the surrounding lattice is perturbed, what results in highly localized breakdown without collateral material damage¹⁰. However, it is well recognized that reversing the writing direction should not affect material processing and associated modifications.

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2. QUILL WRITING

Recently it was noticed that the regions of glass irradiated by femtosecond laser pulses with intensities from a certain range exhibit anisotropic scattering¹¹, reflection and negative birefringence^{12, 13}. It was shown that 3D self-assembled sub-wavelength planar structures, aligned perpendicular to the polarization direction of the writing laser are responsible for these peculiar optical properties. While analyzing the conditions for nanograting formation, it was noticed that moving a sample from left to right and vice versa produces different modifications in glass: nanogratings and related form birefringence could be formed only in one scanning direction. The effect resembles writing with a quill pen and is interpreted in terms of anisotropic trapping of the electron plasma by a tilted front of the ultrashort laser pulse.

Experiments were performed with a regeneratively amplified mode-locked Ti:Sapphire laser system (Coherent RegA 9000) generating 150 fs pulses with a maximum energy of 2.4 μJ at a wavelength of 800 nm and a repetition rate of 250 kHz. The laser radiation in a Gaussian mode was focused via a 50 $\times$ (NA=0.55) objective into the bulk of the sample. A series of lines were then directly written by scanning in alternating directions at a depth of 0.5 mm below the front surface. The writing speed was 200 $\mu\text{m/s}$ and each line was written with only one pass of the laser, with the polarization vector directed perpendicular to the line and pulse energy of 0.9 μJ . After writing, the structures were side-polished and imaged with a scanning electron microscope (SEM). The SEM image exposed tracks elongated in the direction of light propagation due to beam's confocal parameter, and enhanced by self-focusing effects, with a periodic structure in the direction of light polarization (Fig. 1). On closer inspection we were surprised to observe a difference in the structures written in opposite directions. This difference is revealed in small depth variation of the tracks and a tilt of the periodic structures written in the forward and reverse directions. The periodic planar nanostructures were aligned along the direction of the writing laser polarization and were responsible for form birefringence of the irradiated region.

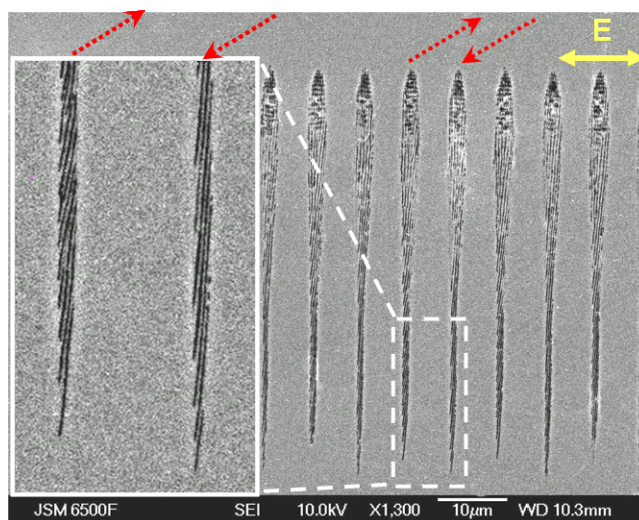


Figure 1. SEM image of cross sections of the structures in glass along light propagation. The distance between lines is 7 μm .

In another experiment a series of lines was written using an IMRA-FCPA $\mu\text{Jewel D-400}$ amplified ytterbium fiber laser system, operating at 1045 nm, with pulse duration <500 fs and repetition rates ranging from 100 kHz to 1 MHz. The high stability of the FCPA laser system is crucial for systematic studies. The polarization of the laser was aligned perpendicular to the writing direction. The lines were written in alternating directions from forward to reverse at different pulse energies (from 0.2 to 1.8 μJ). After writing, laser exposed areas were captured using both crossed-polarized (CP) and Nomarski-DIC illumination (both back-illumination). Composite images (Fig. 2) were created to show the same portion of each feature using the two illumination techniques. With these composite images, the amount of birefringence visible with the CP illumination can be compared with the texture of the feature using the DIC imaging technique. In one of the experiments we wrote 10 groups of 4 lines with alternating writing direction with different repetition rate and speed at each series. The product of repetition rate and writing speed was kept constant, in order to maintain the same total fluence. At low energies, lines written in both directions were the same (Fig. 2, 0.4-0.6 μJ). However, with an increase in energy the appearance of directional dependence (which was strongest at about 0.8-0.9 μJ)

in the written lines was observed. The directional dependence is more clearly seen in the birefringence of the lines. This dependence can also be observed in the morphology (texture) of lines written in opposite directions, with a line written in one direction being rougher than a line written in the reversed direction (Fig. 2a). However, with further increase of energy above a certain threshold value, both lines become uneven with indications of collateral damage, and the birefringence of the lines disappears as well as the directional dependence. We believe that the latter phenomenon can be explained by a cumulative thermal effect¹⁴. This is supported by the presence of modifications with rough features, much bigger than the spot of the beam, at high repetition rates (500 kHz – 1 MHz) and the absence of such features with collateral damage at low repetition rates (below 300 kHz). This agrees with the silica glass heat diffusion time (about 1 μ s). We also tested the dependence of the observed effect on writing speed near the energy threshold of the disappearance of directional phenomenon and observed that the directional dependence becomes stronger at lower writing speeds (Fig. 2b).

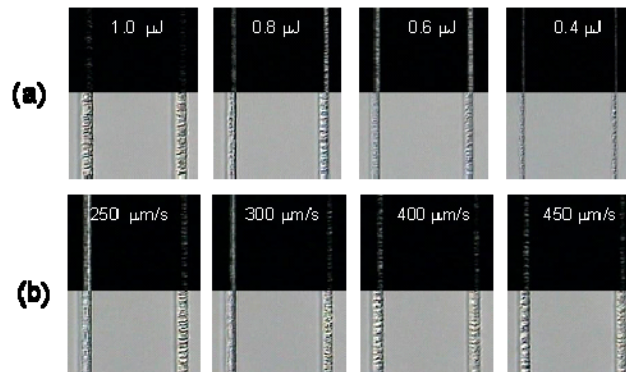


Figure 2. Images in crossed polarizers (dark part) and Nomarski-DIC (light part) of the lines written in glass in opposite directions at repetition rate of 500 kHz with writing speed of 500 μ m/s and different energies and (a) and pulse energy of 0.9 μ J and different writing speeds (b).

When the beam was rotated by 90 degrees, using a two-mirror periscope while other writing parameters were maintained the same including the polarization of the laser beam perpendicular to the stage movement, we observed only weak difference in structures written in opposite directions. This indicates that an asymmetry in the structure of the beam can be responsible for the observed phenomenon.

The other intriguing result is the observation of different textures in the processed material for laser polarizations perpendicular and parallel to the movement of the sample in one direction and the same textures for two polarizations when writing in the opposite direction (Fig. 3a). The SEM images of the cross-sections of the lines revealed a different texture in the lines written in opposite directions (Fig. 3b). Remarkably, the nanograting of about 300 nm period, which is responsible for the form birefringence of irradiated regions, can be seen only in the initial part of cross sections of lines written in one of two directions. This small area is followed by one with a collateral damage due to thermal effect, which correlates with a weak birefringence of these lines. It is also observed, that in almost entire cross sections of the lines, written in opposite direction, there is the nanograting along the direction of light polarization with the period of about 250 nm together with the additional periodicity, along the direction of light propagation, of about 720 nm, which is of the wavelength of light (λ/n , $\lambda = 1045$ nm, $n = 1.45$) (Fig. 3b). These lines demonstrate no evidence of the collateral thermal damage and much stronger birefringence (Fig. 3a). Lines written at a repetition rate of 100 kHz also clearly show different textures in opposite directions, without any evidence of collateral damage due to thermal effect. The SEM images reveal the presence of the nanograting in the direction of light polarization almost in the entire cross section for one writing direction and the nanograting, again with additional periodicity along the propagation direction of about the wavelength of light, for opposite writing direction.

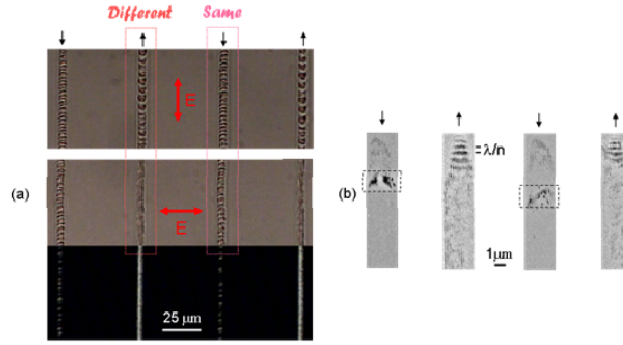


Figure 3. (a) CP and DIC images of the lines written with orthogonal polarizations with 500 kHz repetition rate, writing speed 250 $\mu\text{m/s}$ and pulse energy 0.9 μJ . The difference in texture for two polarizations is observed only for one writing direction. The tilted front of the pulse along writing direction is shown. (b) SEM images of cross sections of lines written with polarization perpendicular to writing direction are also shown. The regions of collateral damage are marked with dashed lines.

The writing anisotropy is observed only at a certain range of pulse energies, which excludes the stage movement as the cause. Inspection of the intensity distribution of the laser beam did not reveal any peculiarities in the shape of the beam, which was close to circular (Gaussian shape). The only possibility left to explain the puzzle of the writing direction anisotropy is related to the anisotropy of the frequency distribution (frequency chirp) in the beam. A spatial frequency chirp and related pulse front tilt is quite common in femtosecond laser systems¹⁵. Even a small delay across the beam that corresponds to $\sim 10\%$ of the pulse duration results in pulse tilt as strong as tens of degrees in the vicinity of the focal plane. The pulse front tilt is enhanced in a dispersive media, as in the case of electron plasma close to plasma frequency, which is formed in the focus of the beam due to multiphoton ionization of glass. The pulse front tilt is a tilt in the intensity distribution in the front of the pulse. It is known, that in the presence of intensity gradients, the charges (e.g. electrons) experience the ponderomotive force (light pressure), which expels the electrons from the region of high intensity¹⁶. Indeed, free electrons are affected by a variation of the laser intensity as they quiver in the electric field of the laser pulse. In the non-relativistic case this can be expressed with the fluid equation of motion in an electromagnetic field by

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{e}{m_e} (\mathbf{v} \times \mathbf{B} + \mathbf{E}), \quad (1)$$

where $\mathbf{v}$ is the electron velocity vector, m_e is the electron mass, e is the electron charge. The ponderomotive force, $\mathbf{F}_p$, follows from this equation by time averaging the electric field as

$$\mathbf{F}_p = -\frac{e^2}{4m_e\omega^2} \nabla E^2 = -\frac{e^2}{2c\epsilon_0 m_e \omega^2} \nabla I, \quad (2)$$

where c is the speed of light in vacuum, ϵ_0 is the permittivity of free space, ω is the frequency of light and I is the light intensity. It is possible to derive a ponderomotive potential, U_p , as

$$U_p = \frac{e^2 I}{2c\epsilon_0 m_e \omega^2}. \quad (3)$$

For very short and intense laser pulses, the ponderomotive force can become very important and the resulting acceleration will tend to push electrons in front of the laser pulse, as a kind of “snow-plough” effect¹⁷. Estimated intensity in the focus of a laser beam in our experiments is of about $3 \times 10^{14} \text{ W/cm}^2$ which will produce ponderomotive potential of 60 meV. This potential is higher than the energy at room temperature, which is of about 40 meV. Electron plasma in our experiments will still experience this kind of force in front of the pulse. Due to the tilt of the intensity distribution, the force will act on the electron plasma along the direction of the intensity gradient. By moving the beam, the ponderomotive force in the front of the pulse will trap and displace the electrons along the direction of movement of the beam and only in one direction corresponding to the tilt in the intensity distribution (we refer to this phenomenon as

the “quill effect”). The electron plasma waves, excited in electron plasma, are responsible for the formation of the nanograting¹³ and self-assembled form birefringence¹⁸. The trapping and displacement of the electrons with the movement of the beam affects the interference of plasma waves, and related form birefringence. The periodic structure, with the period of the wavelength of light, along the direction of light propagation is created as a result of the interference between plasma waves and plasma oscillation. Trapping of the electron plasma damps plasma oscillation and related interference producing longitudinal periodic structure with the wavelength of light. The observed difference in the onset of the collateral thermal damage for two writing directions is also the consequence of the anisotropic tapping effect (Fig. 3b). Further support of the proposed mechanism is the evidence of different textures of modified material for writing with light polarizations parallel and perpendicular to the movement in one of writing directions (Fig. 3a). This observation is explained by the difference in boundary conditions for two orthogonal polarizations at the interface of the tilted pulse front along the writing direction.

The spatial chirp and the related pulse front tilt can change significantly along the beam propagation direction. For the interpretation of the experimental results measurements of the pulse front tilt in the focus of the beam are necessary¹⁹. However, currently such measurements cannot be realized due to small spot size and high light intensity in the focus of the beam. However, further experiments confirmed that indeed the pulse front tilt can be used to control material modifications and in particular as a new tool for laser processing and optical manipulation, e.g. for achieving calligraphic style of laser writing, when the appearance of a “stroke” varies in relation to its direction.

The experiments were carried with an amplified, mode-locked Ti:Sapphire laser operating at 800 nm wavelength with 70 fs pulse duration and a 250 kHz repetition rate was used in the first experiment. The linearly polarized laser beam was focused via a 50× (NA = 0.8) objective at a depth of 60 μm beneath the surface of the fused silica sample. Line structures were written inside the bulk material by translating the sample perpendicularly to the light propagation direction, using a linear motorized stage (Aerotech ALS-130). After irradiation, the sample was inspected using an optical microscope. The first group of lines was written by scanning in alternating directions inside the sample with the pulse energy of 2.6 μJ and the scan speed of 50 μm/s (Fig. 4a). The temporal characteristic of the pulses, in particular the pulse front tilt before the focusing objective, were characterized using a GRENOUILLE device (8.50 Model)¹⁵. The measured pulse front tilt for the first group of lines was 4×10^{-2} fs/mm. As shown in Figure 4a, the directional dependence can be clearly observed in the morphology of the lines written in opposite directions, with a line written in one direction being rougher than a line written in the reversed direction. The directional dependence can also be revealed by imaging the lines between crossed polarizers, in which only the smooth lines written in one direction show birefringence. Next the pulse front tilt was reversed by tuning the pulse compressor to the value of -8.64×10^{-2} fs/mm and the second group of lines was imprinted by scanning in alternating directions (Fig. 4b). Comparing the structures written with the opposite sign of the pulse front tilt, the mirror change in the induced modifications becomes evident (Fig. 4). This experiment unambiguously demonstrates that the directional dependence of the writing process and the induced modification is determined by the pulse front tilt of the femtosecond laser pulses.

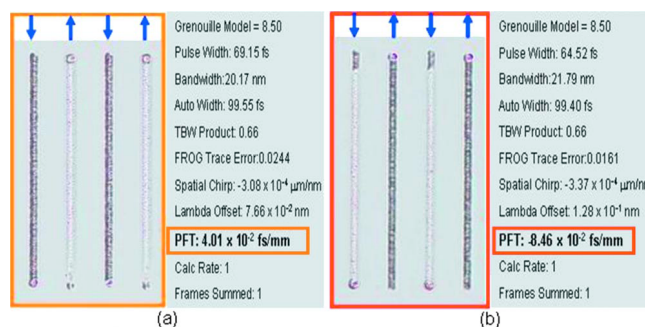


Figure 4. Microscope bright field image of the line structures written using femtosecond pulses with positive pulse front tilt (a) or negative pulse front tilt (b). The distance between the lines is 25 μm. The writing direction is shown by the arrow. The respective screen shots containing measured laser pulse parameters by GRENOUILLE device are shown.

Moreover, when the pulse energy was increased to 3 μJ and above, both lines revealed type 3 modifications and the birefringence in the induced structures disappeared. The latter result indicates that the threshold energy for creating type 3 modification inside fused silica depends not only on the pulse energy but also on the writing direction. For example,

the line structures, written toward the top (Fig. 4a), reveal higher threshold energy for the type 3 modifications than the structures written in the opposite direction. This threshold dependence reverses when the sign of the pulse front tilt is changed (Fig. 4b). Furthermore, no directional dependence could be observed when the pulse front tilt was minimized by tuning the pulse compressor. It should be highlighted that the quill writing effect depends strongly on the focusing depth of the laser irradiation under the sample surface. Changing the focusing depth by only 10%, which is from 60 to 55 or 65 μm , completely eliminated the quill writing effect and produced type 2 or type 3 structures in both directions.

An alternative experiment was also carried out to provide additional evidence that the pulse front tilt is responsible for the quill writing effect. A laser source, producing pulses of 150 fs duration at 250 kHz repetition rate and 800 nm, was used in this experiment. The laser beam profile, measured using a BeamScan system (Photon Inc.), had a well defined Gaussian shape. A 50 $\times$ (NA = 0.55) objective was used to focus laser beam at a depth of 120 μm beneath the surface of the sample. The optimum depth for the quill effect in this experiment was different from the previous one due to the difference in laser beam parameters in the two experiments. The group of four lines with alternating writing directions was imprinted with the pulse energy of 1.4 μJ and scan speed of 50 $\mu\text{m/s}$ (Fig. 5a). One additional mirror was added in the setup to reverse the direction of the pulse front tilt before writing the next group of lines (Fig. 5b). In this writing, configuration the second group of four lines was imprinted with all other writing parameters identical to the previous experiment. It was observed that the structural modifications in the lines of the second group were mirrored when compared with the lines of the first group. This result provides further evidence that the pulse front tilt is responsible for the directional dependence in the ultrafast laser writing.

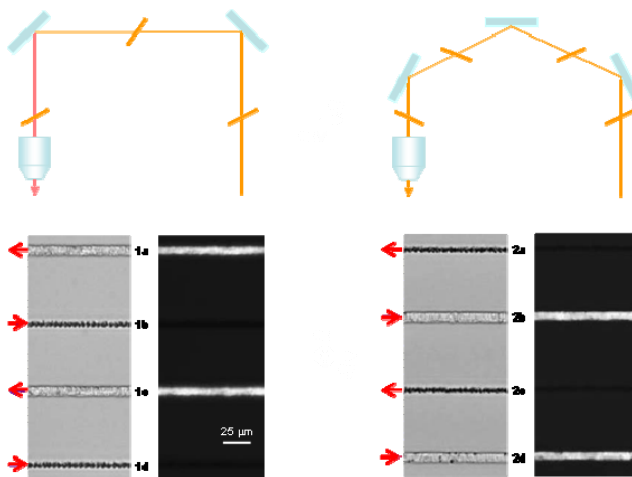


Figure 5. “Quill” effect – lines written in opposite directions have different morphology. In crossed polarizers one can clearly see that birefringent modification is induced only in one direction. The effect can be reversed by reversing tilt direction by reflecting beam from a mirror.

We also observed strong white light emission (400–700 nm) corresponding to type 3 structural modifications and a weaker emission corresponding to the nanogratings formation. This difference was reproducible in different writing experiments. Supercontinuum generation can be excluded as the explanation of this emission because the length of light propagation in the focus of high NA objective is too small to produce a significant spectral broadening. The observed white emission might be related to thermal radiation, e.g. bremsstrahlung radiation, which emitted by electron plasma heated to thousands of degrees at high light intensities (10^{14} W/cm^2)²⁰.

3. ANISOTROPIC BUBBLE FORMATION

Another intriguing result is the observation of anisotropic directional cavitation in the irradiated region when the pulse energy was increased to the level of 2.4 μJ (Fig. 6). Bubbles with diameters of about 1–2 μm were formed on the sides of the irradiated line structures and about 10 μm upstream from the focus of the beam towards the laser (Fig. 6a). When the writing direction was reversed, the bubbles were shifted towards one side from the centre of the beam (Fig. 6b). The bubbles have a lower refractive index in the centre and higher refractive index in the surrounding which indicates that these bubbles are cavities or voids surrounded by a densified material. Moreover, the bubbles show different colour under transmission microscopy which could be explained by the interference due to the light reflected at the front and at

the back side of a bubble. The formation of multiple bubbles in the plane perpendicular to writing direction is difficult to explain by the micro-explosion mechanism^{4, 21}. One should expect a micro-explosion to take place only in the region of highest intensity, which is in the centre of the Gaussian beam. It is likely that the bubbles are created as the result of glass melting followed by cavitation. In femtosecond optical breakdown, laser pulse duration and the thermalization time of the energy of the free electrons are much shorter than the acoustic transit time from the centre of the focus to its periphery. Therefore, no acoustic relaxation is possible during the thermalization time, and the thermo-elastic stresses caused by the temperature rise stay confined in the focal volume, leading to a maximum pressure rise. The tensile stress causes the formation of a cavitation bubble when the rupture strength of the molten glass is exceeded²². The observation of the shift of the bubble formation from the centre of the beam can be explained by the fact that a particle with a refractive index lower than the surrounding medium, such as a void or bubble is repulsed from the region of high intensity in the focus of a Gaussian beam. The component of the tilt, which is orthogonal to the directions of writing and the light propagation, will trap and shift the bubbles towards one side of the imprinted line structure, in a kind of a “snow plough” effect. It should be noted that this effect provides the first evidence of a possibility of manipulation of microscopic objects using pulses with a tilted intensity front.

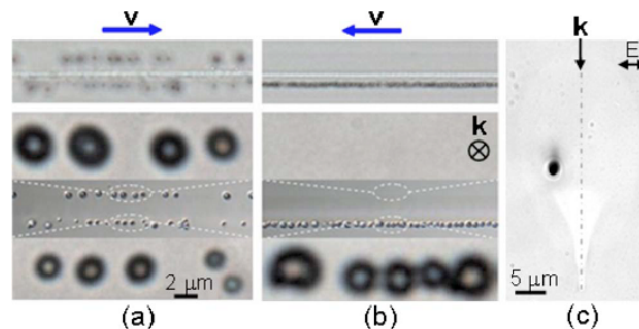


Figure 6. Bight field images with different magnifications of the line structures fabricated in opposite directions (a) and (b) with 2.4 μJ pulse energy and scan speed of 50 $\mu\text{m/s}$. (c) Image of a cross section of the line structure shown in (b).

Surprisingly, the bubble modifications can directly transfer into the birefringent features during the line writing process (Fig. 6). This transition can even be observed during the writing. At a certain distance, typically about 500 μm from the start of writing, the formation of bubbles abruptly terminated. Instead evidence of self-assembled form birefringence appeared and continued until the end of line writing process. The transformation in the type of modification was correlated with the change in intensity of white light emission during the inscription process, which was similar to the emission described above. Strong white light emission during the bubble formation dropped at the modification transition and only weak emission could be observed during the formation of birefringent structures. It should be noted that all writing parameters, including the pulse energy and scanning speed, were kept constant during the encryption process and the phenomenon could be repeated in different areas of the sample. However, there is one parameter which is not constant, in particular the temperature of the whole glass sample, which could increase as a result of light absorption during the writing process. It should be noted that self-assembled form birefringence structures and related nanogratings disappear at temperatures above the glass transition temperature²³. This indicates that local temperature in the irradiated region should drop at modification transition from the glass melting temperature (1715°C), corresponding to the bubble formation, to the temperature below the glass transition temperature (1175°C), corresponding to the nanograting formation. This local temperature decrease can be explained by an increase of the heat capacity caused by the heating of the whole glass sample²⁴. Indeed, given that $\Delta T = \Delta Q / mc_p$, where ΔT is the temperature difference, ΔQ is the heat energy, and m is the mass of the substance, c_p is the heat capacity, the temperature drops when heat capacity increases. The nanograting starts to form once the local temperature has dropped below the glass transition temperature. The energy is consumed by a nanograting formation process, which locks temperature below the glass transition temperature and explains why formation of nanogratings does not stop until the end of writing process.

4. NON-RECIPROCAL WRITING

It has also been a common belief that in a homogeneous medium, the photosensitivity and corresponding light-induced material modifications do not change on the reversal of light propagation direction⁵. However, we have demonstrated

that when the propagation direction of the femtosecond laser beam is reversed from +Z to -Z directions, the structures written in a lithium niobate crystal (LiNbO_3) are mirror images when translating the beam along the +Y and -Y directions (Fig. 7). Thus, the phenomenon of the laser writing in lithium niobate is non-reciprocal, i.e. a single light beam interacts with the crystal differently for opposite directions of light propagation. This experimental finding implies that forward and backward propagating intense light beams interact with the crystal differently resembling conventional Faraday effect. Therefore laser writing in lithium niobate can be seen as a new non-reciprocal nonlinear optical phenomenon.

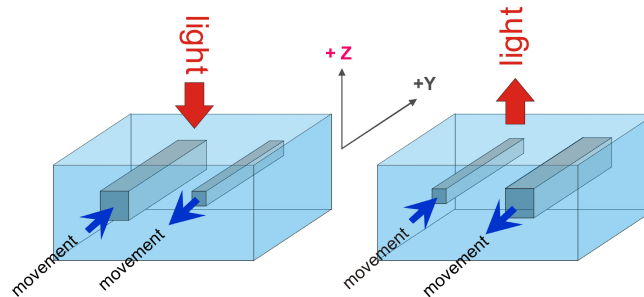


Figure 7. In a non-centrosymmetric medium modification of the material can be different when femtosecond laser beam propagates in opposite directions. Red arrow indicates light propagation direction, blue arrows show direction of sample's movement.

The experiments were performed using a mode-locked, regeneratively amplified Ti:Sapphire laser system (Coherent RegA 9000), operating at 800 nm with 150 fs pulse duration and 250 kHz repetition rate. The linearly polarized laser beam was focused via a 50X objective ($\text{NA} = 0.55$) 150 μm below the surface of a 1 mm thick LiNbO_3 sample. The spot size in the focus of the beam was estimated to be $\sim 2 \mu\text{m}$. The laser polarization was controlled using a half-wave plate and the pulse energy was varied using a neutral density filter. The sample was mounted on a computer controlled linear motorized stage (Aerotech ALS-130). Straight lines of modifications were written by translating the sample perpendicular to the propagation direction of the laser beam. The writing direction is defined as the scan direction of the laser spot with respect to the LiNbO_3 sample.

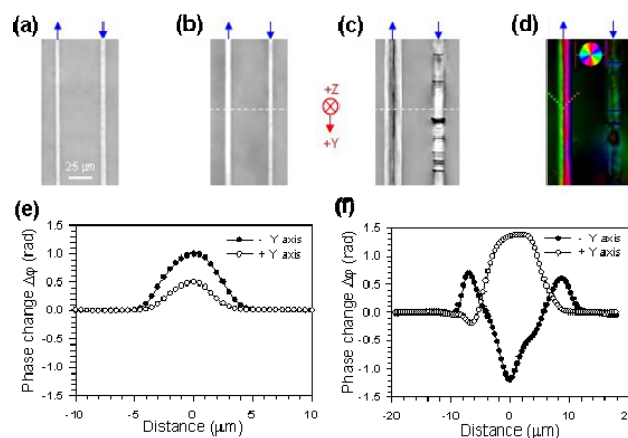


Figure 8. Line structures written along the Y-axis of the LiNbO_3 sample. a-c, QPM phase images of the lines written along the -Y axis and the +Y axis of LiNbO_3 with pulse energies of: 1.2 μJ (a); 1.8 μJ (b); 2.4 μJ (c). d, Quantitative birefringence image of the line structures. The brightness represents the retardance magnitude while the colour represents the slow axis of the birefringence region. The colour of the circular legend shows the direction of slow axis. The dashed lines show the slow axis of the birefringence region. Quantitative phase change profiles of the line structures written along the -Y and +Y axes at the dashed lines in (b) (e) and (c) (f), respectively. Writing directions of the structures in a-d are shown by arrows.

Firstly, groups of lines with various pulse energies ranging from 1 μJ to 2.4 μJ were written below the -Z face of the LiNbO_3 sample. The scan speed was 200 $\mu\text{m}/\text{s}$ and the laser beam was linearly polarized along Y-axis. For each group

two lines were produced with opposite direction, in other words with writing direction along the $-Y$ and $+Y$ axis of LiNbO_3 respectively (Fig. 8). After irradiation, the structural modifications were inspected by quantitative phase microscopy (QPM)²⁵, using an Olympus BX51 optical microscope equipped with a motorized focusing stage (Physik Instrumente). A quantitative phase map of the structures was produced using the QPM software (Iatvia Vision Sciences). The refractive index change of the structure was estimated from $\Delta n = \Delta\phi\lambda/(2\pi d)$, where $\Delta\phi$ is the phase shift of the light at wavelength of 550 nm and d is the thickness of the structure along the light propagation direction. The stress region was analyzed using quantitative birefringence imaging system (CRi Abrio Imaging System).

We observed different material modifications depending on the pulse energy and the writing direction. For the lines written in both directions with pulses energies below 1.4 μJ , a positive phase change and thus a positive index change is created in the exposed region (Fig. 8a). The lines have the width of 2.5 μm , which is close to the focal spot size of the laser beam. No difference was observed for the lines written in the opposite directions. The lines imprinted with pulses energies between 1.4 μJ to 2 μJ still have a positive index change in both directions (Fig. 8b). However, we observed the appearance of directional dependence in the structures written along the $-Y$ and the $+Y$ axis of LiNbO_3 . The difference is firstly revealed in the morphology of the line structures. The lines inscribed along the $-Y$ axis of LiNbO_3 have a larger width than those along the $+Y$ axis (Fig. 8b). In addition, the directional difference can also be revealed from the phase change in the structures. The lines written along the $-Y$ axes of LiNbO_3 produce a larger positive phase change than those along the $+Y$ axis (Fig. 8e).

With further increase of pulse energy above 2 μJ , this dependence could even be distinguished from the textures of the lines written in opposite directions. Some optical damage regions appeared in the lines written along the $+Y$ axis of LiNbO_3 (Fig. 8c). In contrast, no damage could be observed in the whole line written along the $-Y$ axis. The phase change ($\Delta\phi$) profile of the lines is shown in Fig. 8f. As a result, the line inscribed along the $+Y$ axis still has a positive phase change, similar to those created with lower pulse energies, and exhibits a maximum $\Delta\phi$ of 1.4 rad. By assuming the length of the structure along the Z axis of about 30 μm , the maximum Δn is 4×10^{-3} . However, the line written along the $-Y$ axis exhibits a more complex phase change profile. A central dip region shows a negative phase change, while the surrounding regions have a positive phase change. This observation indicates that femtosecond laser modification results in a negative refractive index change of the central exposed region and a positive index change of the surrounding region. Stressed regions created as a result of the expansion of the material at the focus of the writing laser beam can account for the positive index change of the surrounding region²⁶⁻²⁸. This was confirmed by the quantitative birefringence imaging of the line structures (Fig. 8d). The line created along the $-Y$ axis of the sample shows two birefringent regions surrounding the central irradiated region and the slow axis of the birefringent region is inclined about 45° toward the writing direction. The amorphization of the focal volume and subsequent stress induced birefringence could account for this type of modification. In contrast, no birefringence features could be observed in the structures written along the $+Y$ axis. It is also noted that the birefringence becomes weaker when the pulse energy is decreasing and no birefringence could be observed when the pulse energy was below 2 μJ . Moreover, the directional dependence does not depend on the laser polarization. Compared to the structures imprinted when the crystal was translated along the Y -axis, no directional dependence has been observed when the structures were written by translating the crystal along the X -axis (Fig. 9). This indicates that the directional dependence of the light-induced modifications in LiNbO_3 is associated with the crystal symmetry.

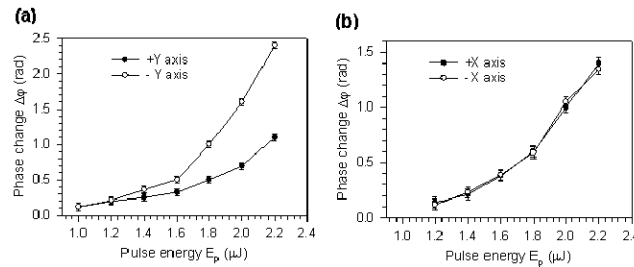


Figure 9. Comparison the line structures imprinted along the Y -axis and along the X -axis. a-b, Measured phase change of the line structures versus pulse energies for the lines written along the Y -axis of the LiNbO_3 sample (a) and the X -axis of the LiNbO_3 sample (b). The error bar is due to the variation of phase value for the unexposed region of the LiNbO_3 sample

To verify that the directional dependence of the modifications along the Y axis of LiNbO_3 is defined by the crystal axes, four groups of lines were fabricated in the sample. Two groups of the lines with opposite writing directions, along the $-Y$ and $+Y$ axis respectively, were written inside the sample with the pulse energies of $2.4\ \mu\text{J}$ and $2\ \mu\text{J}$. (Fig. 10a). The sample was then rotated by 180° around the Z axis and another two groups of structures, with the same writing parameters including the direction of the stage movement, was then imprinted in the sample (Fig. 10b). By comparing Figs 10a and 10b one can observe that the modification of the crystal structure is determined by the orientation of the writing direction with respect to the Y axis of the crystal.

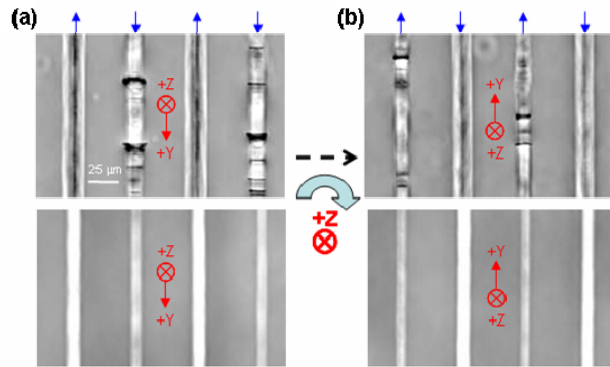


Figure 10. Phase images of line structures in the rotation experiment. a-b, QPM phase images of lines imprinted along the Y axis with $2.4\ \mu\text{J}$ (top) and $2\ \mu\text{J}$ (bottom) pulse energies. The lines were written before (a) and after rotating by 180° around the Z-axis (b) of the crystal respectively.

Secondly, groups of structures were written by the laser beam propagating along the $+Z$ (Fig. 11a) and the $-Z$ (Fig. 11b) axes of the crystal. As expected, the created structures were different for writing directions along the $+Y$ and $-Y$ axes of the sample. However, we were surprised to observe a mirror change in the structural modifications in this case, when the propagation direction of the writing beam is reversed. Indeed, in contrast to the lines, written along the $+Y$ axis with $2.4\ \mu\text{J}$ pulse energy by the beam propagating along $+Z$ axis, which showed the optical damage features (Fig. 11a), no damage could be observed in the lines imprinted with the same fabrication parameters by the beam propagating along $-Z$ axis (Fig. 11).

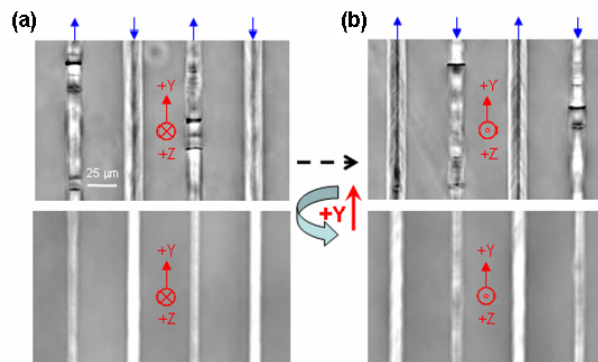


Figure 11. Phase images of line structures in the flip experiment. a-b, QPM phase images of lines written along the Y axis with $2.4\ \mu\text{J}$ (top) and $2\ \mu\text{J}$ (bottom) pulse energies. The lines were written by propagating the laser beam along the $+Z$ axes (a) and the $-Z$ axes (b) of the crystal respectively.

The change in the structural modifications between these lines is only produced by reversing the propagation direction of the focused laser beam with respect to the Z axis of the crystal. Moreover, the modification features, which appeared previously in the line written along the $+Y$ axis by focusing below the $-Z$ face of the crystal could only be observed in the line written along the $-Y$ axis when focusing below the $+Z$ face. Therefore a mirror change of the modifications in two similar structures written along the Y axis ($+Y$ and $-Y$ directions) with the reversed beam propagating direction along the Z axis is discovered. Similar mirror change of phase profiles was also observed for the line structures without

strong damage features written with the pulse energy of 2 μJ . We also used different writing speeds and observed that the line width increases with reducing the scan speed. This indicates that a heat accumulation effect takes place during the writing process.

Groups of line structures were also written in Z-cut LiNbO₃ sample using the picosecond laser system (Lumera Super Rapid), operating at 1064 nm with 9 ps pulse duration, 250 kHz repetition rate and with pulse energies comparable to those used with the femtosecond laser system. Modifications with crack features were observed at the same fluencies and at intensities of about one order of magnitude lower compared to the femtosecond laser system and with no evidence of the non-reciprocal writing phenomenon. This indicates that the phenomenon is accompanying only ultrashort pulses, possibly due to higher intensities which could be achieved with femtosecond pulses without strong damage of the sample.

It should be noted that the directional asymmetry of ultrashort-pulse-light-induced modifications in glass (femtosecond laser quill writing effect) does not depend on the orientation of a medium or the direction of light propagation and can be controlled by the tilt of a pulse front. In contrast to glass, the directional dependence of writing in lithium niobate depends on the orientation of a crystal with respect to direction of the beam movement and the light propagation direction. Specifically, the created structures possess a strong anisotropy only when the focused beam is translated along the Y axis, while no anisotropy is observed when the beam is translated along the X axis. The mirror symmetry of the structures created by the light beam propagating along the +Z and -Z axes of the crystal (see Fig. 11) indicates that the phenomenon observed in LiNbO₃ is not relevant to the tilt of the pulse front, as is the of femtosecond laser quill writing effect in glass. We show in the following that, in a crystalline medium, even the pressure produced by a non-tilted pulse front can result in dependence of the created structures on both the direction of writing and the propagation direction of the laser beam.

A heat current J , which is carried by the electrons of plasma created by the femtosecond laser pulse, and generated by the ponderomotive force and the photon drag effect, can be phenomenologically presented in the following form:

$$J_i = \eta_{ijklmn} E_j E_k^* \nabla_n (E_l E_m^*) + i \zeta_{ijklmn} E_j E_k E_l^* E_m^* k_n \quad (4)$$

where subscripts label Cartesian indices, E is the complex amplitude of the light electric field, i. e. $E_k E_l^*$ is proportional to the light intensity and is responsible for heating via the plasma absorption. The first and second term in the right-hand-side of Equation (4) describe pressure created by the front of the pulse and photon drag effect²⁹, respectively, η_{ijklmn} and $\zeta_{ijklmn} = \zeta_{ikjlmn} = \zeta_{ilmjkn}$ are sixth rank tensors, k is wave vector. When the light beam propagates along the Z axis of the lithium niobate crystal, the current along the X axis is identically zero by symmetry, while that along the Y axis has symmetry allowed components of tensors η_{ijklmn} and ζ_{ijklmn} . For example, for the Y-polarized light beam, the thermal current along the Y-axis given by the following equation:

$$J_y = \left(\eta_{yyyyyz} \frac{\partial |E_y|^2}{\partial z} + ik \zeta_{yyyyyz} |E_y|^2 \right) |E_y|^2 \quad (5)$$

We will refer this phenomenon as the photothermal effect in noncentrosymmetric media or the bulk photothermal effect in order to highlight that the light-induced heat current can be excited even under homogeneous illumination and in a homogeneous noncentrosymmetric medium³⁰.

However, the developed phenomenological description of the observed effect does not explain why the heat current produced by laser beam can manifest itself in the modification of a moving sample. The major difficulty here is that the timescales of these processes are very different. Specifically, the laser field, which drives the heat current, described by Eq. (4), is around for only about 150 fs. The created electrons in the laser-produced plasma thermally equalize with lattice in few picoseconds and finally recombine with nearby ions in few nanoseconds or even faster. From the other hand, at the pulse repetition rate of 250 kHz, the time interval between laser pulses is at least one thousand times longer. What is there that "remembers" what direction the laser beam is being translated in 4 microseconds later, when the next laser pulse arrives?

The short answer is that anisotropic energy distribution created by the short lasting current described by Eq. (4) is finally imprinted in the anisotropy of lattice temperature across the irradiated area. This can be seen as more efficient heating

of the material when subsequent pulses arrive in a region where the electric-field driven heat current has already pushed thermal energy from another part of the beam due to the crystal anisotropy. To clarify this, we would like to recall that our experiments were performed in the so-called thermal accumulation regime³¹. In this regime, the material temperature is determined by the cumulative effect of many laser pulses. This is because, in our experimental conditions (beam diameter $d = 2 \mu\text{m}$, thermal diffusivity $D = \kappa/\rho c_p \approx 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, thermal conductivity $\kappa \approx 2 \text{ W mK}^{-1}$, specific heat capacity $c_p \approx 714 \text{ J kg}^{-1} \text{ K}^{-1}$, volume mass density $\rho \approx 4640 \text{ kg m}^{-3}$, pulse repetition rate $f = 250 \text{ kHz}$, sample velocity $v = 200 \mu\text{m s}^{-1}$), the effective cooling time $\tau_c = d^2/D \approx 4 \mu\text{s}$ coincides with $1/f$ and the thermal diffusion length $L_D = (4D/f)^{1/2} \approx 4 \mu\text{m}$ is comparable with the beam diameter. The distance traveled by the sample between two consecutive pulses $h = v/f = 0.8 \text{ nm}$, i.e. the number of laser pulses overlapping within the beam diameter is $N = d/h = 2,500$. Such a small beam shift between two pulses implies that the beam movement can be considered as continuous.

The absorption of the laser radiation results in the average heat production within the focus area with the rate

$$\left(\frac{\partial Q}{\partial t} \right)_{\text{hom}} = a(\tau_p \times f)I \quad (6)$$

where I is the laser intensity, τ_p is the pulse duration, and a is determined by the absorption coefficient, volume of the irradiated area etc. This heating homogeneously increases the temperature within the whole focal area. However, in the LiNbO₃, focal area where exists an average heat current along the Y axis (Eq. 4): of

$$\overline{J_y} = b(\tau_p \times f)I^2 \quad (7)$$

where b is determined by relevant non-zero components of the material tensors introduced in Eq.(4). When the light beam is propagated along Z-axis of the crystal, this flow will push the heat along Y-axis at the transfer rate

$$\left(\frac{\partial Q}{\partial t} \right)_{\text{anisotropic}} = A \overline{J_y} \quad (8)$$

where A is the cross-section of the irradiated area in the XZ-plane. This heat transfer will produce the temperature difference between opposite sides of the beam:

$$\Delta T = \frac{d}{\kappa A} \left(\frac{\partial Q}{\partial t} \right)_{\text{anisotropic}} = \frac{d}{\kappa} \overline{J_y} \quad (9)$$

The sign of ΔT depends on the parameter b , i.e. on the relevant component of the material tensor responsible for the observed effect. In particular, if the laser beam is Y-polarized and $\text{Im}\{\zeta_{yyyyyz}\} > 0$, then $J_y < 0$. Therefore, if the Y-axis is horizontal with negative direction on the right, the temperature of the right-hand side of the irradiated area will be higher than that of the left-hand side (Fig. 11). In such a case the direction of the beam movement along the Y-axis does matter. Specifically, the temperature of the crystal when beam is translated along Y-axis in the negative direction will be always higher than that when the beam is translated along Y-axis in the positive direction.

The mechanism of this direction-dependent writing can be visualized using the simplified model presented in Fig. 11. In this model, for sake of simplicity we assume that the beam movement is discontinuous, i.e. that the beam movement along Y-axis consists of jumps at length equal to its diameter. The conventional absorption described by Eq. (6) produce homogeneous heating of the irradiated area at temperature T_0 . If no other heating mechanisms are present, the temperature is the same for any position of the beam and does not depend in which direction we move the beam. However, if the anisotropic heating mechanism described by Eq. (7) is involved, the temperature at the right side of the beam is higher than that of the left-hand side by $\Delta T = dJ_y/\kappa$. When the beam jumps right (to the negative direction of the Y-axis) to its next placement, the temperature of the left side of the beam increases to $T + \Delta T$, while the temperature of the right side of the beam is T . The anisotropic heating mechanism is switched on and increases the temperature of the right side so that it will be by ΔT higher than that of the left side of the beam. As a result the temperature of the right side of the beam will be equal to $T + 2\Delta T$. The same temperature increase will happened after next jump. After m jumps in the

direction that coincides with the direction of the anisotropic heat flow, the temperature of the very right irradiated area will be equal to

$$T_{parallel}^{max} = T_0 + \frac{md}{\kappa} \times \overline{J}_y \quad (10)$$

When the light beam moves in the positive direction along Y-axis, the temperature of the left-side of the beam is the same after each jump. Therefore, although the anisotropic heating mechanism results in the increase of the temperature of the right-side of the beam, the temperature of the crystal does not increase (Fig. 12):

$$T_{opposite}^{max} = T_0 + \frac{d}{\kappa} \times \overline{J}_y \quad (11)$$

Therefore, the anisotropic heating may result in drastically different scenario of the laser writing, which we refer as differential heating of the sample. This increase of the temperature described by Eq. 10 will eventually slow down due to thermal diffusion and melting of the sample. Moreover uneven heating of the sample when the beam moves opposite to the heat flow, which is described by Eq. (11) and illustrated in Fig. 12, may results in a shock-induced damage, which is evident for one of the writing directions (Figs. 10 and 11). Apparently in the real experimental conditions, situation is more complicated because we need to account for interplay of the thermal diffusion and accumulation; however the simplified model above well illustrates how anisotropic heating can manifest itself in the crystal modification by a moving laser beam.

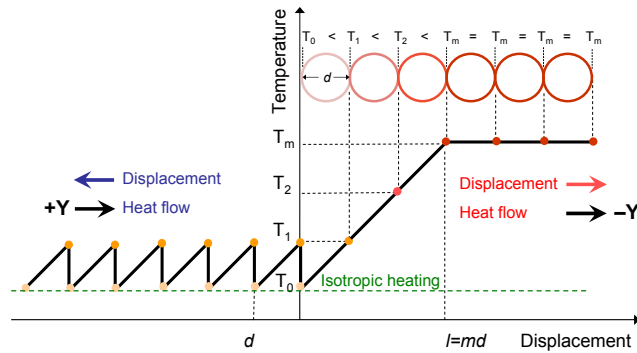


Figure 12. Illustration of the differential heating of a crystal as a result of the bulk photothermal effect. Heat flows in the $-Y$ direction of the crystal (black arrow). Temperature of the crystal increases till saturation when the beam is displaced in the direction of heat flow (red arrow) and oscillates near the level defined by isotropic heating (green line) when displacement is opposite to the heat flow (blue arrow). Big circles illustrate the laser beam and darker colour corresponds to higher temperature of the sample in the position of the beam.

The restrictions imposed on the light-induced current by crystalline symmetry explain the observed directional dependence of writing. Specifically, since the light beam propagated along the Z axis does not produce thermal current along the X axis, the crystal modification is not sensitive to the translation of the light beam along the X axis. In contrast, when the beam is translated along the Y axis, the in-plane heat flow is either parallel or anti-parallel to the beam velocity. Since the heating of crystal is stronger when the direction of the heat flow coincides with direction of the beam movement, the modification of the non-centrosymmetric crystal shows a pronounced directional dependence independently on the pulse front tilt. It should be also noted, that we observed similar crystal modifications for the X- and Y-polarized beams. Such an experimental finding is also supported by crystal symmetry because in the LiNbO_3 crystal, the thermal current along Y-axis is not forbidden for both X- and Y-polarized beams, however the current is described by different independent components of the material tensor. The similarity of the crystal modifications just indicates that these components are of the same order in magnitude.

One can observe from Eqs. (4, 5) that interplay of the crystal anisotropy and light-induced heat flow gives rise to a new non-reciprocal nonlinear optical phenomenon, the nonreciprocal photosensitivity. In the lithium niobate, the nonreciprocal photosensitivity manifests itself as changing the sign of the light-induced heat current when light

propagation direction is reversed. This phenomenon is visualized when the modification of the crystal is performed by a moving light beam; in such a case the created pattern is mirrored when light propagation direction is reversed.

5. CONCLUSIONS

In conclusion, it is remarkable that a laser beam, one of the most modern writing tools, could be used for calligraphic inscription similar to writing with a quill pen, which is based on the anisotropy of a quill's tip shape. Moreover, modifications of materials by light span from photosynthesis and photography to material processing and laser writing and there are only few parameters of the light beam which control material transformations, in particular wavelength, intensity, polarization, exposure time and pulse duration. Our results add one more parameter to this list – direction of beam movement or pulse front tilt.

Also the first realization of non-reciprocal ultrafast laser writing in Z-cut lithium niobate crystal was demonstrated using a tightly focused ultrafast laser beam. We discovered that when the direction of the laser beam is *reversed* from +Z to –Z directions, the structures written in the crystal when translating the beam along the +Y and –Y directions are *mirrored*. Therefore, a single light beam interacts with the crystal differently for opposite directions of light propagation. This new non-reciprocal nonlinear optical phenomenon is interpreted in terms of light pressure at the front of ultrashort pulse, photon drag effect, and associated light-induced thermal current in crystalline media. We would like to point out that nonreciprocal phenomena are very rare in optics and are usually associated with breaking of the time-reversal symmetry due to the presence of the magnetic field. One may recall conventional Faraday effect and magneto-chiral dichroism³², when interaction of a single light beam with a homogeneous material is different for two opposite directions similarly to the non-reciprocal photosensitivity reported here.

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